CHEMISTRY
AN ASIAN JOURNAL
ACES
FULL PAPER

DOI: 10.1002/asia.201301082

PPh_3-Catalyzed Ring-Expansion Reactions of Sulfamate-Derived Cyclic Imines with Acetylenedicarboxylates

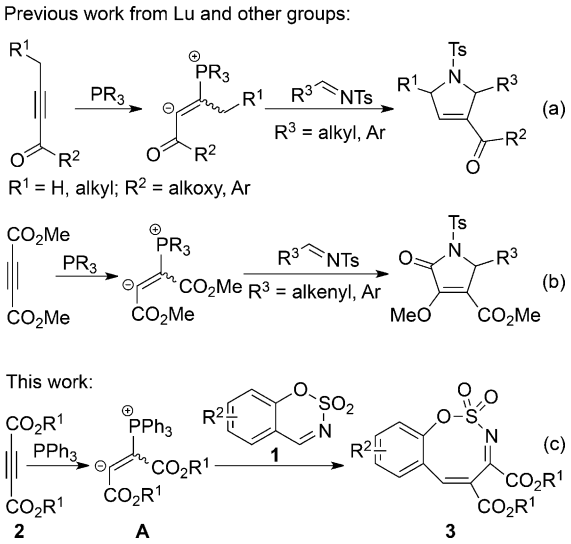
Zhilin Yang,[a] Hao Yu,[a] Lei Zhang,[a] Hang Wei,[a] Yumei Xiao,[a] Lanzhen Chen,[b] and Hongchao Guo*[a]

Abstract: The PPh_3-catalyzed ring-expansion reaction of sulfamate-derived cyclic imines with acetylenedicarboxylates has been developed. The reaction works quite efficiently under very mild conditions to afford benzo[*g*][1,2,3]oxathiazocine-4,5-dicarboxylate 2,2-dioxide derivatives in high yields.

Keywords: heterocycles · imines · organocatalysis · ring expansion · synthetic methods

Introduction

Nucleophilic phosphine organocatalysis has seen much development in the past few decades and has become a powerful tool for the synthesis of acyclic and cyclic compounds.[1] Among various phosphine-catalyzed reactions, the annulation reactions of electron-deficient olefins, allenes, and alkynes with activated imines[2] have received much attention due to their extensive application in the synthesis of various useful nitrogen-containing heterocycles[3] and natural products.[4] Compared with electron-deficient olefins and allenes, alkynes were seldom used in annulation reactions with imines, and only a few examples have been reported. In 1998, Lu and Zu reported Bu_3P-catalyzed [3+2] cycloaddition of 2-butynoate with *N*-tosylimines (Scheme 1a) and Ph_3P-catalyzed [3+2] cycloaddition of dimethyl acetylenedicarboxylate with *N*-tosylimines (Scheme 1b).[2b] Both reactions afforded pyrrolidine derivatives as products in high yields. Ten years later, Xue and co-workers extended this chemistry to Bu_3P-catalyzed [3+2] cycloaddition of alkynyl ketones with *N*-tosylimines providing highly functionalized pyrrolidines in good to excellent yields with complete stereoselectivity (Scheme 1a).[2n] For the reactions in Scheme 1a, because the alkynes have a γ-carbon atom, both alkynyl ester and alkynyl ketone served as C_3 synthons under phosphine-catalysis conditions. In Scheme 1b, acetylenedicarboxylate functioned as a C_3 synthon in phosphine-catalyzed reactions with imines. In general, contrary to alkynyl esters with γ-carbon atoms, acetylenedicarboxylate acts as a C_2 synthon in annulation reactions mediated by Lewis bases.[1c]



Scheme 1. Reactions of activated alkynes with activated imines.

Normally, the reaction of an acetylenedicarboxylate with an electron-deficient imine would result in a [2+2] cycloadduct. Since phosphine-catalyzed [2+2] cycloaddition reactions are extremely rare,[5] it is very attractive to investigate [2+2] cycloaddition of acetylenedicarboxylates with cyclic imines as a new type of annulation reaction. Moreover, phosphine-catalyzed annulation of activated alkynes with cyclic imines has never been reported. On the other hand, biologically active compounds containing a sulfamate moiety displayed significant biological activities, such as antibiotic, antibacterial, antiviral, antimetastatic, anticonvulsant, anticancer, anti-obesity, anti-arthritis, and anti-osteoporosis activity,[6] and thus the sulfamate moiety is often used as an important pharmacophore in drug design. The devel-

[a] Z. Yang, H. Yu, L. Zhang, H. Wei, Dr. Y. Xiao, Dr. H. Guo
Department of Applied Chemistry
Institution China Agricultural University
2 West Yuanmingyuan Road, Beijing 100193 (China)
Fax: (+86) 10-6281-5579
E-mail: hchguo@cau.edu.cn

[b] L. Chen
Bee Research Institute
Chinese Academy of Agricultural Sciences
Beijing 100093, China

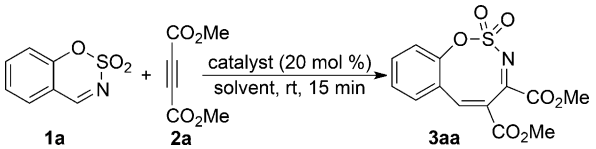
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/asia.201301082.

opment of new reactions for the synthesis of the biological compounds with a sulfamate moiety is highly desirable. In this context, we carried out the annulation reaction of sulfamate-derived cyclic imines **1** with acetylenedicarboxylates **2**. Unexpectedly, an interesting ring-expansion reaction was found (Scheme 1c). Herein, we report this new PPh_3-catalyzed ring expansion reaction of sulfamate-derived cyclic imines **1** with acetylenedicarboxylates **2** to give sulfamate-fused benzo[*g*][1,2,3]oxathiazocine-4,5-dicarboxylate 2,2-dioxide derivatives under mild conditions (Scheme 1c).[7]

Results and Discussion

The sulfamate-derived cyclic imines **1**[8] were used as the substrates for phosphine-catalyzed reactions. Initially, we investigated the cycloaddition of cyclic imine **1a** with dimethyl acetylenedicarboxylate (**2a**). In the presence of PPh_3 (20 mol%), treatment of **1a** with 1.2 equiv of **2a** in dichloromethane at room temperature gave a 61% yield of ring-expansion product **3aa** (Table 1, entry 1), which was identified

Table 1. Ring-expansion reaction of cyclic imine **1a** with acetylenedicarboxylate **2a**.[a]



Entry	Catalyst	Solvent	Yield[b] [%]
1	PPh_3	CH_2Cl_2	61
2	PPh_3	toluene	77
3	PPh_3	benzene	93
4	PPh_3	THF	68
5	PPh_3	AcOEt	62
6	PPh_3	acetone	55
7[c]	DMAP[d]	benzene	63
8[c]	DBU[e]	benzene	–
9[c]	DABCO[f]	benzene	–
10[c]	Et_3N	benzene	–

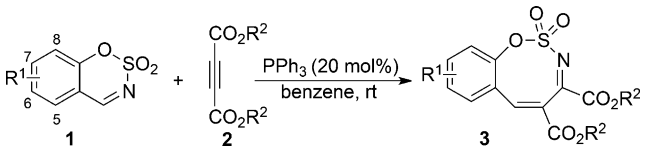
[a] 1.2 equiv of **2a** were used. [b] Yields of isolated products. [c] The reaction time was 72 h. [d] 4-Dimethylaminopyridine. [e] 1,8-Diazabicyclo-[5.4.0]undec-7-ene. [f] 1,4-Diazabicyclo[2.2.2]octane.

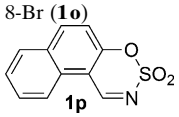
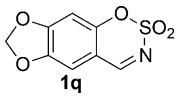
by NMR spectroscopy. A small amount of a more polar compound was also observed and isolated in less than 5% yield.[9] Solvent screening indicated that the best-performing solvent was benzene, and afforded the product **3aa** in 93% yield (Table 1, entry 3). DMAP could also catalyze the reaction to give the product **3aa** in 63% yield (Table 1, entry 7),

Abstract in Chinese:

发展了三苯基膦催化的乙炔二羧酸酯与氨基磺酸酯衍生的环状亚胺之间的扩环反应。这个反应可在温和条件下高效地进行，能以高产率得到苯并八元[杂环化合物。

Table 2. Substrate scope.[a]



Entry	R^1 in **1**	R^2	*t*	Product	Yield[d] [%]
1	H (**1a**)	Me (**2a**)	15 min	**3aa**	93
2	6-Me (**1b**)	Me (**2a**)	13 min	**3ba**	98
3	6-OMe (**1c**)	Me (**2a**)	1 h	**3ca**	80
4	6-*t*Bu (**1d**)	Me (**2a**)	12 min	**3da**	91
5	6-F (**1e**)	Me (**2a**)	25 min	**3ea**	91
6	6-Cl (**1f**)	Me (**2a**)	25 min	**3fa**	95
7	6-Br (**1g**)	Me (**2a**)	5 min	**3ga**	90
8[b]	7-MeO (**1h**)	Me (**2a**)	1 h	**3ha**	91
9	7-Cl (**1i**)	Me (**2a**)	4 min	**3ia**	92
10	7-Br (**1j**)	Me (**2a**)	4 min	**3ja**	73
11[c]	8-Me (**1k**)	Me (**2a**)	5 min	**3ka**	97
12	8-OMe (**1l**)	Me (**2a**)	5 min	**3la**	92
13[c]	8-*t*Bu (**1m**)	Me (**2a**)	2 h	**3ma**	91
14[c]	8-Cl (**1n**)	Me (**2a**)	15 min	**3na**	83
15[c]	8-Br (**1o**)	Me (**2a**)	2 h	**3oa**	86
16[c]	 **1p**	Me (**2a**)	9 h	**3pa**	65
17[b,c]	 **1q**	Me (**2a**)	72 h	**3qa**	57
18	H (**1a**)	Et (**2b**)	1 h	**3ab**	97
19	H (**1a**)	*i*Pr (**2c**)	1 h	**3ac**	92

[a] 1.2 equiv of acetylenedicarboxylate were used. [b] The reaction was carried out at 40 °C. [c] 40 mol% PPh_3 was used. [d] Yields of isolated products.

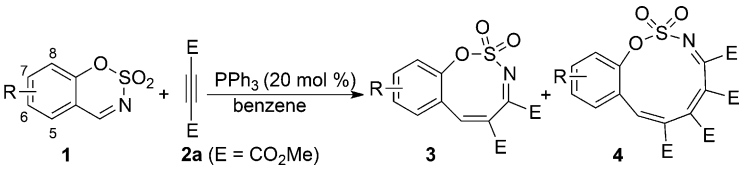
but other Lewis bases such as DBU, DABCO, and Et_3N were ineffective (Table 1, entries 8–10).

With PPh_3 as catalyst and benzene as solvent, reactions of various cyclic imines **1** with acetylenedicarboxylates **2** were evaluated (Table 2). The corresponding ring-expansion products were obtained in 57–98% yield. The results showed that introducing various substituents, including electron-donating and electron-withdrawing groups, into the 6- or 7-position of the cyclic imines did not influence the yields of their reactions with **2a** (Table 2, entries 2–10). The reactions were quite fast and were complete in less than 30 min at room temperature in most cases. However, 6-MeO-substituted cyclic imine **1c** required a longer time to give the product **3ca** in 80% yield (Table 2, entry 3), and 7-MeO-substituted substrate **1h** required elevated temperature and a longer time to furnish the product **3ha** in 91% yield (Table 2, entry 8). Introducing electron-donating or electron-withdrawing substituents in the 8-position of the cyclic imines lowered the activities of the substrates and resulted in 40 mol% of Ph_3P being required to promote the reactions (Table 2, entries 11 and 13–15). Two special substrates (**1p** and **1q**) required an increased amount of PPh_3 (40 mol%) and longer reaction times, and **1q** even required elevated temperature to promote the reaction, and they provided the corresponding products in modest yields (Table 2, entries 16

and 17). Under phosphine-catalysis conditions, diethyl acetylenedicarboxylate (**2b**) and diisopropyl acetylenedicarboxylate (**2c**) could also react with cyclic imine **1a** to afford the corresponding products in 97 and 92% yield, respectively (Table 2, entries 18 and 19). Under the standard conditions, 0.2 g of cyclic imine **1a** was treated with dimethyl acetylenedicarboxylate for 6 min to give **3aa** in 94% yield of isolated product. This demonstrated that the reaction could be a practical method for the synthesis of biologically interesting heterocycles. A byproduct was observed in every case, and increased in amount over time. Therefore, once substrate conversion is almost complete, the reaction must be quenched immediately to prevent generation of the byproduct and decreased yield of the major product.

Next, we studied in detail the byproducts of the abovementioned reactions. By using 2D NMR spectroscopy, they were determined to be benzo[*i*][1,2,3]oxathiazecine-4,5,6,7-tetracarboxylate 2,2-dioxide derivatives **4**, formed from two molecules of acetylenedicarboxylate and a cyclic imine. Imines **1d**–**1f** were chosen as substrates to investigate the generation process of byproducts **4** (Table 3).[10] The reaction

Table 3. Study on the side reaction.[a]

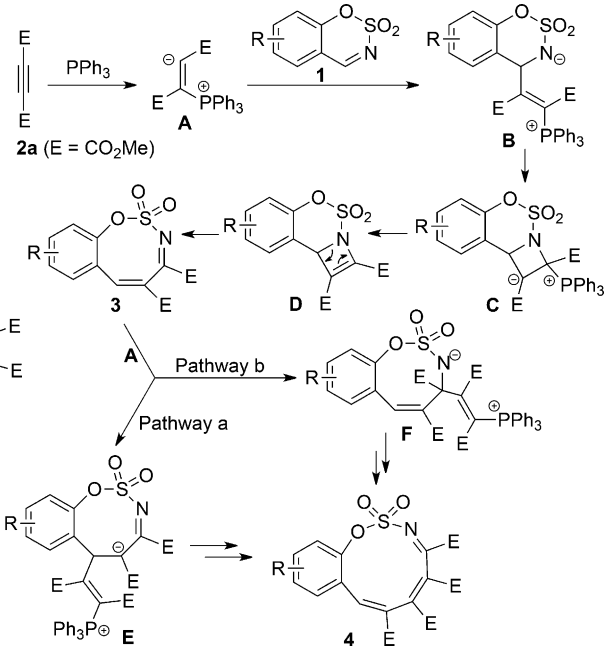


Entry	R in **1**	*T* [°C]/*t* [min]	**3**, Yield[b] [%]	**4**, Yield[b] [%]
1	6-*t*Bu (**1d**)	25/12	**3da**, 91	**4da**, 8
2	6-*t*Bu (**1d**)	25/15	**3da**, 65	**4da**, 33
3	6-*t*Bu (**1d**)	0/60	**3da**, 75	**4da**, 0
4	6-*t*Bu (**1d**)	0/105	**3da**, 92	**4da**, 6
5	6-*t*Bu (**1d**)	0/120	**3da**, 64	**4da**, 35
6	6-F (**1e**)	40/60	**3ea**, 70	**4ea**, 29
7	6-Cl (**1f**)	25/60	**3fa**, 62	**4fa**, 36

[a] 1.5 equiv of acetylenedicarboxylate were used. [b] Yields of isolated products.

of cyclic imine **1d** with 1.5 equivalents[11] of acetylenedicarboxylate **1a** was carried out at room temperature in benzene with 20 mol% of PPh_3. When the reaction was quenched after 12 and 15 min, compound **4da** was isolated in 8 and 33% yield, respectively (Table 3, entries 1 and 2). As the reaction was too fast at room temperature, it was difficult to track. To monitor the reaction more easily by TLC, it was carried out at 0°C. After 60 min, about 80% of substrate **1d** was converted, the product **3da** was isolated in 75% yield, but product **4da** was not observed (Table 3, entry 3). At the moment substrate **1d** was almost exhausted, compound **4da** appeared. After the reaction proceeded for 120 min, **3da** and **4da** were isolated in 64 and 35% yield, respectively (Table 3, entry 5). Compound **4da** was probably formed by the reaction of **3da** with acetylenedicarboxylate **2a**. In fact, under otherwise identical conditions, pure product **3da** was treated with 1.2 equivalents of acetylenedicarboxylate **2a** to give **4da** in 27% yield, although **3da** was not fully converted to **4da**. For substrates **1e** and **1f**, 29 and 36% yield of the corresponding compounds **4ea** and **4fa** was obtained, respectively (Table 3, entries 6 and 7). The above results showed that, under phosphine-catalysis conditions, cyclic imine **1** is more reactive than product **3** toward acetylenedicarboxylates.

According to reported mechanistic studies on nucleophilic phosphine catalyzed reactions and the experimental observations,[1] a plausible mechanism was proposed for the reactions of the cyclic imines **1** and acetylenedicarboxylate **2a** (Scheme 2). Zwitterion **A**, formed by conjugate addition of



Scheme 2. Proposed mechanism for PPh_3-catalyzed ring-expansion reactions of cyclic imines with acetylenedicarboxylates.

PPh_3 to acetylenedicarboxylate **2a**, undergoes addition to imines to generate sulfamate **B**. Intramolecular conjugate addition of the sulfamate to the phosphonium enoate motif of intermediate **B** followed by elimination of PPh_3 leads to [2+2] cycloadduct **D** and regeneration of PPh_3 catalyst. Ring expansion of intermediate **D** from a four- to an eight-membered ring, which would relieve the ring strain and is enthalpically favorable, provides benzo[*g*]-[1,2,3]oxathiazocine-4,5-dicarboxylate 2,2-dioxide derivative **3** as the final product. Once cyclic imine **1** is exhausted, zwitterion **A** attacks the carbon–carbon double bond of product **3** and undergoes conjugate addition to the α,β-unsaturated ester to generate intermediate **E** (pathway a), or zwitterion **A** attacks the carbon–nitrogen double bond of product **3** to give intermediate **F** (pathway b).[12] Intermediate **E** or **F** then undergoes sequential conjugate addition, expulsion of the PPh_3 catalyst, and ring expansion to give compound **4**.

Conclusions

We have developed the phosphine-catalyzed ring-expansion reaction of sulfamate-derived cyclic imines and acetylenedicarboxylates. The reaction is operationally simple, proceeds smoothly under very mild reaction conditions, and provides various sulfamate-fused benzo[*g*][1,2,3]oxathiazocine-4,5-dicarboxylate 2,2-dioxide derivatives in moderate to excellent yields. Further efforts to expand the scope of phosphine-catalyzed reactions of sulfamate-derived cyclic imines are underway.

Experimental Section

General information

All reactions were performed under an air atmosphere in oven-dried Schlenk tubes with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Benzene solvent was used without any purification. IR spectra were recorded with a Bruker Optics TENSOR 27 instrument. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker 300 spectrometer. High-resolution (HR) ESI mass spectra were recorded with an Agilent instrument on samples dissolved in CH_3CN.

*General procedure for the ring expansion reactions of cyclic imines (**1**) with acetylenedicarboxylates (**2**)*

Acetylenedicarboxylate **2** (0.30 mmol) and benzene (2 mL) were added to a solution of the cyclic imine **1** (0.25 mmol), triphenylphosphine (0.05 mmol), and benzene (4 mL) at room temperature in an oven-dried 15 mL Schlenk tube. The mixture was stirred at room temperature (or the given temperature) for the given time and then concentrated. The residue was purified by flash column chromatography (EtOAc/petroleum ether) to afford the corresponding cycloaddition product.

*Dimethyl benzo[g][1,2,3]oxathiazocine-4,5-dicarboxylate 2,2-dioxide (**3aa**)*

93% yield; white solid; IR (film): $\tilde{\nu}_{max}$ = 2958, 1726, 1597, 1552, 1437, 1396, 1280, 1252, 1189, 1162, 1130, 1085, 1016, 862, 842, 771, 743, 551 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.78–7.70 (m, 1H), 7.51–7.44 (m, 1H), 7.40–7.31 (m, 2H), 7.29 (s, 1H), 3.82 (s, 3H), 3.69 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.0, 163.2, 162.5, 153.4, 138.3, 137.2, 133.8, 128.6, 126.0, 118.9, 115.9, 53.7, 52.9 ppm; HRMS (ESI): *m*/*z* calcd for $C_{13}H_{11}NNaO_7S^+$: 348.0148 [*M*+Na]$^+$; found: 348.0149.

*Dimethyl 8-methylbenzo[g][1,2,3]oxathiazocine-4,5-dicarboxylate 2,2-dioxide (**3ba**)*

98% yield; white solid; m.p. 176–177 °C; IR (film): $\tilde{\nu}_{max}$ = 2960, 1746, 1718, 1601, 1559, 1482, 1437, 1390, 1317, 1282, 1252, 1209, 1187, 1134, 1083, 1014, 862, 823, 770, 735, 720, 700, 668, 615, 579, 527 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55–7.49 (m, 1H), 7.29 (s, 1H), 7.24 (d, *J* = 8.5 Hz, 1H), 7.21–7.17 (m, 1H), 3.83 (s, 3H), 3.71 (s, 3H), 2.38 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.0, 163.3, 162.7, 151.6, 138.4, 138.1, 136.1, 133.8, 128.2, 118.7, 115.7, 53.7, 52.9, 20.8 ppm; HRMS (ESI): *m*/*z* calcd for $C_{14}H_{13}NNaO_7S^+$: 362.0305 [*M*+Na]$^+$; found: 362.0307.

*Dimethyl 8-methoxybenzo[g][1,2,3]oxathiazocine-4,5-dicarboxylate 2,2-dioxide (**3ca**)*

80% yield; white solid; m.p. 130–131 °C; IR (film): $\tilde{\nu}_{max}$ = 2957, 2924, 2850, 1727, 1620, 1585, 1537, 1507, 1461, 1437, 1390, 1343, 1256, 1217, 1198, 1163, 1132, 1084, 1021, 991, 956, 894, 846, 788, 737, 669, 645, 580, 498 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29–7.25 (m, 3H), 6.88–6.81 (m, 1H), 3.83 (s, 3H), 3.81 (s, 3H), 3.71 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.9, 163.3, 162.6, 156.8, 147.2, 138.3, 133.9, 123.0, 120.0, 116.4, 112.3, 56.0, 53.7, 52.9 ppm; HRMS (ESI): *m*/*z* calcd for $C_{14}H_{13}NNaO_8S^+$: 378.0254 [*M*+Na]$^+$; found: 378.0256.

*Dimethyl 8-tert-butylbenzo[g][1,2,3]oxathiazocine-4,5-dicarboxylate 2,2-dioxide (**3da**)*

91% yield; white solid; IR (film): $\tilde{\nu}_{max}$ = 2961, 1728, 1600, 1558, 1437, 1395, 1261, 1192, 859, 835, 787 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.77 (dd, *J* = 2.4, 8.8 Hz, 1H), 7.35 (d, *J* = 2.4 Hz, 1H), 7.31 (s, 1H), 7.28 (d, *J* = 8.8 Hz, 1H), 3.83 (s, 3H), 3.70 (s, 3H), 1.29 ppm (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.0, 163.3, 162.3, 151.4, 149.4, 138.3, 134.8, 134.0, 124.7, 118.5, 115.4, 53.6, 52.9, 34.6, 31.0 ppm; HRMS (ESI): *m*/*z* calcd for $C_{17}H_{19}NNaO_7S^+$: 404.0774 [*M*+Na]$^+$; found: 404.0776.

*Dimethyl 8-fluorobenzo[g][1,2,3]oxathiazocine-4,5-dicarboxylate 2,2-dioxide (**3ea**)*

91% yield; white solid; m.p. 158–160 °C; IR (film): $\tilde{\nu}_{max}$ = 3081, 2960, 1743, 1723, 1606, 1562, 1480, 1440, 1426, 1392, 1321, 1286, 1251, 1234, 1198, 1171, 1124, 1082, 1014, 1000, 920, 885, 857, 831, 772, 535 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49–7.34 (m, 2H), 7.30 (s, 1H), 7.16–7.10 (m, 1H), 3.85 (s, 3H), 3.73 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.3, 172.2, 163.3, 162.3, 160.6, 157.3, 149.50, 149.47, 138.0, 134.2, 124.6, 124.2, 121.0, 120.9, 116.8, 116.7, 114.6, 114.3, 53.8, 53.1 ppm; HRMS (ESI): *m*/*z* calcd for $C_{13}H_{10}FNNaO_7S^+$: 366.0054 [*M*+Na]$^+$; found: 366.0056.

*Dimethyl 8-chlorobenzo[g][1,2,3]oxathiazocine-4,5-dicarboxylate 2,2-dioxide (**3fa**)*

95% yield; white solid; m.p. 171–173 °C; IR (film): $\tilde{\nu}_{max}$ = 2962, 1721, 1598, 1551, 1469, 1436, 1395, 1309, 1277, 1190, 1138,1097, 1081, 1012, 849, 829,804, 768 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68 (dd, *J* = 2.5, 8.8 Hz, 1H), 7.40–7.38 (m, 1H), 7.35–7.31 (m, 1H), 7.30 (s, 1H), 3.86 (s, 3H), 3.74 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.2, 163.3, 162.3, 151.9, 138.0, 136.9, 134.3, 131.4, 127.8, 120.6, 116.9, 53.9, 53.1 ppm; HRMS (ESI): *m*/*z* calcd for $C_{13}H_{10}ClNNaO_7S^+$: 381.9759 [*M*+Na]$^+$; found: 381.9760.

*Dimethyl 8-bromobenzo[g][1,2,3]oxathiazocine-4,5-dicarboxylate 2,2-dioxide (**3ga**)*

90% yield; white solid; m.p. 178–180 °C; IR (film): $\tilde{\nu}_{max}$ = 3444, 2961, 1728, 1600, 1558, 1437, 1395, 1261, 1192, 1145, 1081, 1016, 860, 835, 787, 737, 624, 585, 556 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82 (dd, *J* = 2.4, 8.8 Hz, 1H), 7.53–7.51 (m, 1H), 7.30 (s, 1H), 7.29–7.24 (m, 1H), 3.86 (s, 3H), 3.74 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.0, 163.3, 162.3, 152.4, 139.8, 138.0, 134.3, 130.8, 120.8, 118.6, 117.4, 53.9, 53.1 ppm; HRMS (ESI): *m*/*z* calcd for $C_{13}H_{10}BrNNaO_7S^+$: 425.9254 [*M*+Na]$^+$; found: 425.9238.

*Dimethyl 9-methoxybenzo[g][1,2,3]oxathiazocine-4,5-dicarboxylate 2,2-dioxide (**3ha**)*

91% yield; white solid; m.p. 121–122 °C; IR (film): $\tilde{\nu}_{max}$ = 2958, 2923, 2850, 1725, 1617, 1584, 1534, 1507, 1437, 1382, 1343, 1260, 1189, 1162, 1127, 1083, 1020, 956, 845, 792, 738, 700, 682, 667, 580 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36 (d, *J* = 8.7 Hz, 1H), 7.25 (s, 1H), 6.85–6.78 (m, 2H), 3.93 (s, 3H), 3.82 (s, 3H), 3.70 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.0, 166.8, 163.3, 162.8, 156.1, 138.4, 133.6, 130.4, 113.5, 109.5, 103.1, 56.3, 53.6, 52.9 ppm; HRMS (ESI): *m*/*z* calcd for $C_{14}H_{13}NNaO_8S^+$: 378.0254 [*M*+Na]$^+$; found: 378.0253.

*Dimethyl 9-chlorobenzo[g][1,2,3]oxathiazocine-4,5-dicarboxylate 2,2-dioxide (**3ia**)*

92% yield; white solid; m.p. 121–122 °C; IR (film): $\tilde{\nu}_{max}$ = 3093, 2960, 1727, 1595, 1543, 1481, 1438, 1397, 1263, 1193, 1149, 1094, 1073, 1014, 914, 887, 844, 793, 772, 740, 715, 691, 630, 569, 532 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.35 (m, 2H), 7.34–7.27 (m, 2H), 3.83 (s, 3H), 3.72 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.3, 163.2, 162.4, 153.9, 143.3, 138.1, 134.2, 129.5, 126.6, 119.5, 114.6, 53.8, 53.0 ppm; HRMS (ESI): *m*/*z* calcd for $C_{13}H_{10}ClNNaO_7S^+$: 381.9759 [*M*+Na]$^+$; found: 381.9758.

*Dimethyl 9-bromobenzo[g][1,2,3]oxathiazocine-4,5-dicarboxylate 2,2-dioxide (**3ja**)*

73% yield; white solid; m.p. 129–131 °C; IR (film): $\tilde{\nu}_{max}$ = 3094, 2958, 1725, 1595, 1541, 1478, 1437, 1396, 1263, 1204, 1187, 1148, 1090, 1067, 1015, 989, 901, 844, 793, 770, 743, 626, 566 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.55–7.53 (m, 1H), 7.50–7.45 (m, 1H), 7.31 (d, J = 8.4 Hz, 1H), 7.29 (s, 1H), 3.83 (s, 3H), 3.72 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.5, 163.2, 162.4, 153.6, 138.1, 134.2, 131.7, 129.5, 129.4, 122.5, 114.9, 53.8, 53.1 ppm; HRMS (ESI): m/z calcd for $C_{13}H_{10}BrNNaO_7S^+$: 425.9254 $[M+Na]^+$; found: 425.9263.

*Dimethyl 10-methylbenzo[g][1,2,3]oxathiazocine-4,5-dicarboxylate 2,2-dioxide (**3ka**)*

97% yield; white solid; m.p. 172–173 °C; IR (film): $\tilde{\nu}_{max}$ = 2958, 2373, 2334, 1725, 1590, 1567, 1438, 1383, 1279, 1224, 1195, 1168, 1129, 1047, 875, 839, 769, 742 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.61–7.54 (m, 1H), 7.33–7.20 (m, 3H), 3.81 (s, 3H), 3.69 (s, 3H), 2.43 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.3, 163.3, 162.6, 151.8, 138.7, 138.6, 133.6, 128.8, 126.2, 125.3, 115.7, 53.6, 52.9, 14.7 ppm; HRMS (ESI): m/z calcd for $C_{14}H_{13}NNaO_7S^+$: 362.0305 $[M+Na]^+$; found: 362.0305.

*Dimethyl 10-methoxybenzo[g][1,2,3]oxathiazocine-4,5-dicarboxylate 2,2-dioxide (**3la**)*

92% yield; white solid; m.p. 143–144 °C; IR (film): $\tilde{\nu}_{max}$ = 2958, 2848, 1726, 1593, 1567, 1479, 1459, 1439, 1394, 1331, 1277, 1228, 1195, 1174, 1144, 1069, 1014, 902,871, 839, 807, 764, 735, 686, 590, 551 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.32–7.21 (m, 3H), 7.03–6.98 (m, 1H), 3.97 (s, 3H), 3.81 (s, 3H), 3.69 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.3, 163.3, 162.6, 148.8, 143.1, 138.5, 133.7, 125.7, 119.31, 119.29, 116.6, 56.6, 53.7, 52.9 ppm; HRMS (ESI): m/z calcd for $C_{14}H_{13}NNaO_8S^+$: 378.0254 $[M+Na]^+$; found: 378.0253.

*Dimethyl 10-tert-butylbenzo[g][1,2,3]oxathiazocine-4,5-dicarboxylate 2,2-dioxide (**3ma**)*

91% yield; white solid; m.p. 151–152 °C; IR (film): $\tilde{\nu}_{max}$ = 2960, 1729, 1607, 1586, 1557, 1436, 1395, 1368, 1258, 1200, 1177, 1105, 1033, 1020, 873, 846, 779, 741 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.73 (dd, J = 2.0, 7.5 Hz, 1H), 7.34–7.23 (m, 3H), 3.82 (s, 3H), 3.69 (s, 3H), 1.50 ppm (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.7, 163.3, 162.7, 152.6, 140.7, 138.8, 134.9, 133.6, 126.7, 125.4, 116.7, 53.7, 52.9, 35.1, 29.8 ppm; HRMS (ESI): m/z calcd for $C_{17}H_{19}NNaO_7S^+$: 404.0774 $[M+Na]^+$; found: 404.0772.

*Dimethyl 10-chlorobenzo[g][1,2,3]oxathiazocine-4,5-dicarboxylate 2,2-dioxide (**3na**)*

83% yield; white solid; m.p. 170–172 °C; IR (film): $\tilde{\nu}_{max}$ = 2960, 1723, 1591, 1554, 1438, 1397, 1283, 1257, 1195, 1101, 1019, 802 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.77 (dd, J = 1.7, 7.9 Hz, 1H), 7.39–7.34 (m, 1H), 7.32–7.26 (m, 2H), 3.83 (s, 3H), 3.72 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.7, 163.3, 162.4, 149.7, 138.3, 137.4, 134.2, 126.8, 125.9, 124.5, 117.3, 53.8, 53.1 ppm; HRMS (ESI): m/z calcd for $C_{13}H_{10}ClNNaO_7S^+$: 381.9759 $[M+Na]^+$; found: 381.9759.

*Dimethyl 10-bromobenzo[g][1,2,3]oxathiazocine-4,5-dicarboxylate 2,2-dioxide (**3oa**)*

86% yield; white solid; m.p. 168–169 °C; IR (film): $\tilde{\nu}_{max}$ = 3076, 2960, 1722, 1593, 1549, 1435, 1398, 1374, 1285, 1253, 1194, 1153, 1094, 1016, 866, 843, 809, 791, 771, 735, 683, 584, 553 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.93 (dd, J = 1.4, 8.0 Hz, 1H), 7.45–7.39 (m, 1H), 7.30 (s, 1H), 7.24 (t, J = 8.0 Hz, 1H), 3.83 (s, 3H), 3.72 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.8, 163.3, 162.4, 150.6, 140.5, 138.2, 134.2, 127.6, 126.5, 117.4, 113.0, 53.8, 53.1 ppm; HRMS (ESI): m/z calcd for $C_{13}H_{10}BrNNaO_7S^+$: 425.9254 $[M+Na]^+$; found: 425.9238.

*Dimethyl naphtho[1,2 g][1,2,3]oxathiazocine-2,3-dicarboxylate 5,5-dioxide (**3pa**)*

65% yield; pale yellow solid; m.p. 180–181 °C; IR (film): $\tilde{\nu}_{max}$ = 3442, 2959, 1725, 1621, 1594, 1582, 1527, 1449, 1437, 1394, 1351, 1260, 1193, 1147, 1121, 1064, 1017, 978, 893, 825, 803, 737, 703, 676, 650, 611, 518, 494 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.24–8.13 (m, 2H), 7.98–7.90 (m, 1H), 7.68–7.56 (m, 2H), 7.44 (d, J = 9.0 Hz, 1H), 7.32 (s, 1H), 3.71 (s, 3H), 3.62 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.7, 163.8, 162.8, 155.8, 142.4, 139.4, 134.2, 131.1, 130.04, 129.98, 129.2, 126.9, 123.9, 117.5, 112.9, 53.5, 52.9 ppm; HRMS (ESI): m/z calcd for $C_{17}H_{13}NNaO_7S^+$: 398.0305 $[M+Na]^+$; found: 398.0305.

*Dimethyl [1,3]dioxolo[4′,5′:4,5]benzo[1,2-g][1,2,3]oxathiazocine-4,5-dicarboxylate 2,2-dioxide (**3qa**)*

57% yield; pale yellow solid; m.p. 139–140 °C; IR (film): $\tilde{\nu}_{max}$ = 3439, 1724, 1638, 1527, 1394, 1260, 1193, 1016, 978, 517 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.24 (s, 1H), 6.80 (s, 1H), 6.75 (s, 1H), 6.14 (s, 2H), 3.83 (s, 3H), 3.73 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.9, 163.2, 162.6, 155.0, 151.9, 145.7, 138.5, 133.6, 109.9, 105.6, 103.4, 100.2, 53.7, 52.9 ppm; HRMS (ESI): m/z calcd for $C_{14}H_{11}NNaO_9S^+$: 392.0047 $[M+Na]^+$; found: 392.0047.

*Dimethyl benzo[g][1,2,3]oxathiazocine-4,5-dicarboxylate 2,2-dioxide (**3ab**)*

97% yield; pale yellow solid; m.p. 61–63 °C; IR (film): $\tilde{\nu}_{max}$ = 2986, 1723, 1598, 1553, 1477, 1450, 1397, 1245, 1190, 1161, 1130, 1084, 1028, 977, 862, 771, 618, 551, 515 cm^{-1};^1H NMR (300 MHz, $CDCl_3$): δ = 7.77–7.69 (m, 1H), 7.51–7.45 (m, 1H), 7.38–7.31 (m, 2H), 7.26 (s, 1H), 4.28 (q, J = 7.1 Hz, 2H), 4.13 (q, J = 7.1 Hz, 2H), 1.22 (t, J = 7.1 Hz, 3H), 1.12 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.2, 162.8, 162.1, 153.4, 138.3, 137.1, 133.9, 128.6, 125.8, 118.9, 116.2, 63.0, 62.3, 13.7, 13.5 ppm; HRMS (ESI): m/z calcd for $C_{15}H_{15}NNaO_7S^+$: 376.0461 $[M+Na]^+$; found: 376.0460.

*Dimethyl benzo[g][1,2,3]oxathiazocine-4,5-dicarboxylate 2,2-dioxide (**3ac**)*

92% yield; colorless transparent solid; m.p. 73–74 °C; IR (film): $\tilde{\nu}_{max}$ = 2985, 2939, 1717, 1648, 1598, 1554, 1468, 1452, 1399, 1251, 1190, 1147, 1130, 1103, 1083, 1035, 982, 900, 862, 804, 772, 717, 690, 617, 552, 516, 473 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.77–7.69 (m, 1H), 7.48 (dd, J = 1.6, 8.1 Hz, 1H), 7.39–7.31 (m, 2H), 7.21 (s, 1H), 5.16–5.06 (m, 1H), 5.01–4.90 (m, 1H), 1.21 (d, J = 6.2 Hz, 6H), 1.09 ppm (d, J = 6.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.4, 162.4, 161.8, 153.5, 138.3, 137.1, 134.1, 128.7, 125.8, 118.9, 116.5, 71.3, 70.5, 21.4, 21.2 ppm; HRMS (ESI): m/z calcd for $C_{17}H_{19}NNaO_7S^+$: 404.0774 $[M+Na]^+$; found: 404.0772.

*Tetramethyl 10-chlorobenzo[i][1,2,3]oxathiazecine-4,5,6,7-tetracarboxylate 2,2-dioxide (**4fa**)*

M.p. 155–156 °C; IR (film): $\tilde{\nu}_{max}$ = 2958, 1730, 1623, 1598, 1554, 1470, 1437, 1400, 1325, 1257, 1192, 1154, 1134, 1105, 1026, 889, 863, 831, 797, 771, 737, 703, 582, 523 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.96 (s, 1H), 7.66 (dd, J = 2.5, 8.8 Hz, 1H), 7.31 (d, J = 8.8 Hz, 1H), 7.08 (s, 1H), 3.90 (s, 3H), 3.83 (s, 3H), 3.70 (s, 3H), 3.67 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.4, 163.6, 162.7, 162.3, 151.7, 142.3, 136.4, 133.1, 131.4, 128.8, 120.1, 117.8, 77.2, 53.70, 53.67, 53.3, 52.6 ppm; HRMS (ESI): m/z calcd for $C_{19}H_{16}ClNNaO_{11}S^+$: 524.0025 $[M+Na]^+$; found: 524.0025.

Acknowledgements

This study was supported by the National Natural Science Foundation of China (No. 21172253), the Program for New Century Excellent Talents in University (No. NCET-11-0481), the National Scientific and Technology Supporting Program of China (No. 2011BAE06B05-5), the National S&T Pillar Program of China (2012BAK25B03), Chinese Universities Scientific Fund (No. 2013J002 and 2013RC023), and Nutrichem.

[1] For selected reviews on nucleophilic phosphine organocatalysis, see: a) X. Lu, C. Zhang, Z. Xu, *Acc. Chem. Res.* **2001**, *34*, 535; b) J. L. Methot, W. R. Roush, *Adv. Synth. Catal.* **2004**, *346*, 1035; c) V. Nair, R. S. Menon, A. R. Sreekanth, N. Abhilash, A. T. Biju, *Acc. Chem. Res.* **2006**, *39*, 520; d) L.-W. Ye, J. Zhou, Y. Tang, *Chem. Soc. Rev.* **2008**, *37*, 1140; e) S. E. Denmark, G. L. Beutner, *Angew. Chem.* **2008**, *120*, 1584; *Angew. Chem. Int. Ed.* **2008**, *47*, 1560; f) C. E. Aroyan, A. Dermenci, S. J. Miller, *Tetrahedron* **2009**, *65*, 4069; g) B. J. Cowen, S. J. Miller, *Chem. Soc. Rev.* **2009**, *38*, 3102; h) A. Marinetti, A. Voituriez, *Synlett* **2010**, 174; i) K. Beata, *Cent. Eur. J. Chem.* **2010**, 1147; j) Y. Wei, M. Shi, *Acc. Chem. Res.* **2010**, *43*, 1005; k) S.-X. Wang, X. Y. Han, F. R. Zhong, Y. Q. Wang, Y. X. Lu, *Synlett* **2011**, 2766; l) Q.-Y. Zhao, Z. Lian, Y. Wei, M. Shi, *Chem. Commun.* **2012**, *48*, 1724; m) S. Yu, S. Ma, *Angew. Chem.* **2012**, *124*, 3128; *Angew. Chem. Int. Ed.* **2012**, *51*, 3074.

[2] For selected examples, see: a) Z. Xu, X. Lu, *Tetrahedron Lett.* **1997**, *38*, 3461; b) Z. Xu, X. Lu, *J. Org. Chem.* **1998**, *63*, 5031; c) X. F. Zhu, J. Lan, O. Kwon, *J. Am. Chem. Soc.* **2003**, *125*, 4716; d) G.-L. Zhao, M. Shi, *Org. Biomol. Chem.* **2005**, *3*, 3686; e) R. P. Wurz, G. C. Fu, *J. Am. Chem. Soc.* **2005**, *127*, 12234; f) X.-F. Zhu, C. E. Henry, O. Kwon, *Tetrahedron* **2005**, *61*, 6276; g) G. L. Zhao, M. Shi, *J. Org. Chem.* **2005**, *70*, 9975; h) L. Jean, A. Marinetti, *Tetrahedron Lett.* **2006**, *47*, 2141; i) A. Scherer, J. A. Gladysz, *Tetrahedron Lett.* **2006**, *47*, 6335; j) N. Fleury-Brégeot, L. Jean, P. Retailleau, A. Marinetti, *Tetrahedron* **2007**, *63*, 11920; k) B. Zhang, Z. He, S. Xu, G. Wu, Z. He, *Tetrahedron* **2008**, *64*, 9471; l) G.-N. Ma, F.-J. Wang, J. Gao, M. Shi, *Chem. Commun.* **2008**, *44*, 4998; m) S. Zheng, X. Lu, *Org. Lett.* **2008**, *10*, 4481; n) L.-G. Meng, P. Cai, Q. Guo, S. Xue, *J. Org. Chem.* **2008**, *73*, 8491; o) Y.-Q. Fang, E. N. Jacobsen, *J. Am. Chem. Soc.* **2008**, *130*, 5660; p) N. Pinto, N. Fleury-Brégeot, A. Marinetti, *Eur. J. Org. Chem.* **2009**, 146; q) X. Y. Guan, M. Shi, *J. Org. Chem.* **2009**, *74*, 1977; r) M. Schuler, D. Duvvuru, P. Retailleau, J.-F. Betzer, A. Marinetti, *Org. Lett.* **2009**, *11*, 4406; s) K. Lu, O. Kwon, *Org. Synth.* **2009**, *86*, 212; t) H. Xiao, Z. Chai, C.-W. Zheng, Y.-Q. Yang, W. Liu, J.-K. Zhang, G. Zhao, *Angew. Chem.* **2010**, *122*, 4569; *Angew. Chem. Int. Ed.* **2010**, *49*, 4467; u) H. Liu, Q. Zhang, L. Wang, X. Tong, *Chem. Commun.* **2010**, *46*, 312; v) D. Duvvuru, J.-F. Betzer, P. Retailleau, G. Frison, A. Marinetti, *Adv. Synth. Catal.* **2011**, *353*, 483; w) H. Xiao, Z. Chai, H. F. Wang, X.-W. Wang, D.-D. Cao, W. Liu, Y.-P. Lu, Y.-Q. Yang, G. Zhao, *Chem. Eur. J.* **2011**, *17*, 10562; x) J. Tian, R. Zhou, H. Sun, H. Song, Z. He, *J. Org. Chem.* **2011**, *76*, 2374.

[3] a) S. Castellano, H. D. G. Fiji, S. S. Kinderman, M. Watanabe, P. De Leon, F. Tamanoi, O. Kwon, *J. Am. Chem. Soc.* **2007**, *129*, 5843; b) M. Watanabe, H. D. G. Fiji, L. Guo, L. Chan, S. S. Kinderman, D. J. Slamon, O. Kwon, F. Tamanoi, *J. Biol. Chem.* **2008**, *283*, 9571; c) J. Lu, L. Chan, H. D. G. Fiji, R. Dahl, O. Kwon, F. Tamanoi, *Mol. Cancer Ther.* **2009**, *8*, 1218; d) J. Choi, K. Mouillesseauex, Z. Wang, H. D. G. Fiji, S. S. Kinderman, G. W. Otto, R. Geisler, O. Kwon, J.-N. Chen, *Development* **2011**, *138*, 1173; e) Z. Wang, S. Castellano, S. S. Kinderman, C. E. Argueta, A. B. Beshir, G. Fenteany, O. Kwon, *Chem. Eur. J.* **2011**, *17*, 649; f) D. Cruz, Z. Wang, J. Kibbie, R. Modlin, O. Kwon, *Proc. Natl. Acad. Sci. USA* **2011**, *108*, 6769.

[4] a) Y. S. Tran, O. Kwon, *Org. Lett.* **2005**, *7*, 4289; b) M. Sampath, P.-Y. B. Lee, T.-P. Loh, *Chem. Sci.* **2011**, *2*, 1988; c) I. P. Andrews, O. Kwon, *Chem. Sci.* **2012**, *3*, 2510.

[5] a) X.-Y. Chen, R.-C. Lin, S. Ye, *Chem. Commun.* **2012**, *48*, 1317; b) X.-Y. Chen, S. Ye, *Eur. J. Org. Chem.* **2012**, 5723; c) T. Wang, X.-Y. Chen, S. Ye, *Tetrahedron Lett.* **2011**, *52*, 5488.

[6] For some reviews, see: a) J.-Y. Winum, A. Scozzafava, J.-L. Montero, C. T. Supuran, *Med. Res. Rev.* **2005**, *25*, 186; b) J.-Y. Winum, A. Scozzafava, J.-L. Montero, C. T. Supuran, *Expert Opin. Ther. Pat.* **2006**, *16*, 27; c) L. W. L. Woo, A. Purohit, B. V. L. Potter, *Mol. Cell. Endocrinol.* **2011**, *340*, 175; d) S. J. Williams, *Expert Opin. Ther. Pat.* **2013**, *23*, 79.

[7] For our recent papers on annulation reactions, see: a) R. S. Na, C. F. Jing, Q. H. Xu, H. Jiang, X. Wu, J. Y. Shi, J. C. Zhong, M. Wang, D. Benitez, E. Tkatchouk, W. A. Goddard III., H. C. Guo, O. Kwon, *J. Am. Chem. Soc.* **2011**, *133*, 13337; b) C. F. Jing, R. S. Na, B. Wang, H. L. Liu, L. Zhang, J. Liu, M. Wang, J. C. Zhong, O. Kwon, H. C. Guo, *Adv. Synth. Catal.* **2012**, *354*, 1023; c) J. Liu, H. L. Liu, R. S. Na, G. Y. Wang, M. Wang, J. C. Zhong, H. C. Guo, *Chem. Lett.* **2012**, *41*, 218; d) R. S. Na, Z. Li, H. L. Liu, J. Liu, M. A. Wang, M. Wang, J. C. Zhong, H. C. Guo, *Tetrahedron* **2012**, *68*, 2349; e) X. Wu, R. S. Na, H. L. Liu, J. Liu, M. Wang, J. C. Zhong, H. C. Guo, *Tetrahedron Lett.* **2012**, *53*, 342; f) L. Zhang, C. F. Jing, H. L. Liu, B. Wang, Z. Li, H. Jiang, H. Yu, H. C. Guo, *Synthesis* **2013**, 53.

[8] a) A. Kamal, P. B. Sattur, *Synthesis* **1981**, 272; b) M. Tripathi, D. N. Dhar, *Indian J. Chem. B* **1987**, *26*, 888; c) P. M. Wehn, J. Du Bois, *Org. Lett.* **2005**, *7*, 4685; d) N. D. Litvinas, B. H. Brodsky, J. Du Bois, *Angew. Chem.* **2009**, *121*, 4583; *Angew. Chem. Int. Ed.* **2009**, *48*, 4513; e) Y. Luo, A. J. Carnell, H. W. Lam, *Angew. Chem.* **2012**, *124*, 6866; *Angew. Chem. Int. Ed.* **2012**, *51*, 6762; f) Y. Luo, H. B. Hepburn, N. Chotsaeng, H. W. Lam, *Angew. Chem.* **2012**, *124*, 8434; *Angew. Chem. Int. Ed.* **2012**, *51*, 8309.

[9] As PPh_3 could potentially react with 2 equivalents of acetylenedicarboxylate ina side reaction, a control reaction of PPh_3 with acetylenedicarboxylate was carried out in the absence of cyclic imine. This did not result in the corresponding side product of the reaction. For related work, see: J. B. Hendrickson, R. E. Spenger, J. J. Sims, *Tetrahedron* **1963**, *19*, 707.

[10] The reactions of these three substrates with acetylenedicarboxylate formed sufficient amounts of side product **4** for clear TLC monitoring. The reactions of the other cyclic substrates only produced smaller amounts of **4**.

[11] Using 2.2 equivalents of acetylenedicarboxylate did not increase the yield of side product. Moreover, the reaction generated another unknown side product besides **4**.

[12] To investigate which pathway was followed in the further reaction of products **3**, we performed a cross-reaction of product **3da** with diethyl acetylenedicarboxylate (**2b**). However, a product whose structure is completely different to that of **4da** was obtained. From the structure of this new product, it can not unambiguously be concluded through which pathway products **4** were formed. Experimental details of this reaction and the structure of the new product are given in the Supporting Information.

Received: August 12, 2013
Revised: September 18, 2013
Published online: November 12, 2013